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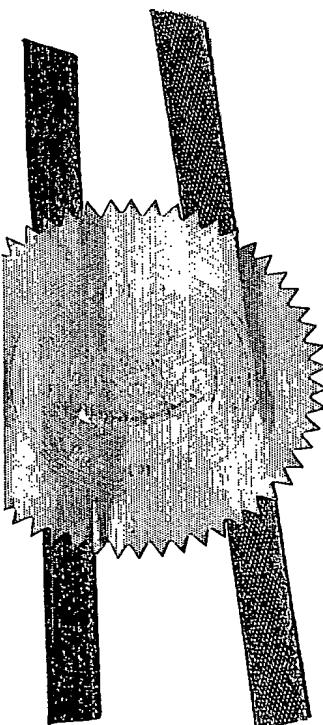
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Title of Invention : THERMALLY RESISTANT ADHESIVE

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PCT REQUEST

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PNL030435WOP

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0	For receiving Office use only	
0-1	International Application No.	PCTMSG 03 / 00104
0-2	International Filing Date	15 APR 2003 (15-04-03)
0-3	Name of receiving Office and "PCT International Application"	REGISTRY OF PATENTS (SINGAPORE) PCT INTERNATIONAL APPLICATION
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0-5	Petition	The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty
0-6	Receiving Office (specified by the applicant)	Intellectual Property Office of Singapore (RO/SG)
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I	Title of invention	THERMALLY RESISTANT ADHESIVE
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PCT REQUEST

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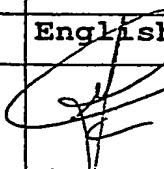
V	Designation of States		
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT (except BG CZ EE HU SI SK TR)	
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	SG	
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary designations	NONE	
VI	Priority claim	NONE	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	3	-
IX-2	Description	7	-
IX-3	Claims	1	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	0	-
IX-7	TOTAL	12	

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	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-EASY diskette	-	Diskette
IX-19	Figure of the drawings which should accompany the abstract		
IX-20	Language of filing of the international application	English	
X	Signature of applicant, agent or common representative		
X-1	Name (LAST, First)	SMIT, Frederik, J.	
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10-1	Date of actual receipt of the purported international application	15 APR 2003 (15-04-03)
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

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11-1	Date of receipt of the record copy by the International Bureau	
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Thermally resistant adhesive

The present invention relates to an adhesive that is suitable for making an electrically conductive connection to a material or system, which is operated at a relatively high temperature. More specifically, the present invention relates to a conductive adhesive that can be used in a heating element. Moreover, the present invention relates to an 5 (electrical) domestic appliance comprising the above adhesive.

A heating element comprising a flat heater system generally comprises two functional layers applied on a substrate, namely an electrically insulating layer and an electrically conductive layer. The function of the insulating layer is to isolate the heat generating layer from the substrate, which may be directly accessible from the outside. The 10 electrically conductive layer in the above-mentioned heating element generally comprises a layer with a high Ohmic resistance, the resistive layer, as well as a layer with a lower Ohmic resistance, which acts as a contacting layer. Heat is generated, by flowing an electrical current through the resistive layer. The layers with high and low Ohmic resistance can be made of different materials, but also of the same material, if the thickness or geometry is 15 adjusted.

In the manufacturing of flat heating elements, insulating and conducting layers are applied on a substrate. For a functional assembly, current carrying wires have to be connected to the contacting layer and, optionally, temperature sensors can be attached. Mechanical attachment, for instance by pressure contacts, has drawbacks like the potential 20 damaging of the layer and a limited contact area. Using conductive adhesives, these drawbacks can be avoided but the demands on the temperature stability of the adhesive are high.

Due to the relatively high working temperatures of the heating elements, which, at the location of the conducting track, easily reach 300°C or more, soldering poses 25 difficulties as standard solder alloys have too low melting temperatures. High melting temperature, hard solder alloys are available for temperatures exceeding 450°C, which is too high for use on aluminium substrates. An alternative approach to the problem is, using a glass frit mixed with conductive particles. In general, the processing of this frit requires too high temperatures, which may damage the insulating or conducting layer or even the substrate if

aluminium, a favorable substrate for heating elements, is used. Frit glasses with lower melting points often contain lead or other potentially toxic metals, which are to be avoided. In addition, the thermal expansion coefficients of these materials do not match the expansion coefficient of aluminium.

5 Epoxy resins comprising silver particles are widely used for low temperature applications, but they do not have good high temperature stability. Poly-dimethylsiloxanes based adhesives have a better temperature resistance but also their temperature stability at working temperatures of 300°C or more is insufficient. Poly-imides have also failed for flat heating applications operating at high temperatures and power densities.

10 The present invention aims to provide for an adhesive that is suitable for making an electrical connection to a material or system, which is operated at a relatively high temperature, and which does not show the above mentioned disadvantages. To this end the present invention provides for an adhesive according to the preamble wherein said adhesive is based on a sol-gel precursor.

15 By using sol-gel precursors high temperature stable connections can be made. Such adhesives, based on a sol-gel precursor can easily be cured by means of heat.

In particular for making conductive connections, the adhesive is based on a sol gel precursor and metal particles.

20 Several sol-gel precursors can be used. For example, the sol gel precursor may comprise a compound from the group of tetraalkoxysilanes, alkyl-alkoxysilanes, phenyl-alkoxysilanes, diphenylalkoxysilanes, the hydrolysed derivatives of said compounds, or combinations thereof.

25 However, in a particular advantageous embodiment of the invention the sol-gel precursor comprises a hybrid sol gel materials based on methyltri(m)ethoxysilane, phenyltri(m)ethoxysilane, and/or diphenyldi(m)ethoxysilane. These materials are known to have excellent temperature resistance and a high chemical stability. These precursors can be reacted with water in the presence of a catalyst to form reactive silanol groups that would react with each other to provide oligomeric and polymeric binder materials. In some cases precursors containing silanol groups rather than alkoxy groups, such as diphenylsilanediol 30 can be used directly.

These precursor materials, in particular methyltri(m)ethoxysilane may also be used in flat heating elements for the conductive layer. In a preferred embodiment methyltri-ethoxysilane (MTES) based binder filled with silver particles is used. This combination of

materials is used for the conductive track and has shown no signs of degradation after 600 hours of active heating with a power density of 20 W/cm^2 at a track temperature of 320°C .

Preferably, the conductive particles comprise silver particles or silver alloy particles. Sol-gel materials, especially methyltrimethoxysilane (MTMS) and methyltriethoxysilane, have shown to stop effectively the migration of silver. Therefore an adhesive based on sol-gel/silver materials will survive the operational demands in a flat heating element.

The use of sol-gel materials is usually restricted to fairly thin layers. For non-hybrid precursors, containing four alkoxy groups, a layer thickness higher than $1 \mu\text{m}$ cannot be obtained. However, for hybrid materials containing three alkoxy groups and one non-hydrolysable group, thicker layers can be achieved. For example with MTES a thickness of 2-3 μm is easily reached. If a hybrid sol-gel system is filled with particles, much thicker layers can be achieved, for instance about $50 \mu\text{m}$ may be used for the insulating layer for a flat heating element and about $10 \mu\text{m}$ may be deposited for the conductive layer. In order to obtain such thick layers, the volume fraction of particles must be carefully controlled. Ideally, the particles are densely packed and all the space in between the particles is filled with binder, in this case a binder derived from a sol gel material. In practice, for commercially available polydisperse powders a volume fraction of particles between 40% and 55% is preferably used. At these volume fractions a high conductivity can be achieved because of the many contacts between the conducting particles.

Although a thickness of about $50 \mu\text{m}$ is fairly thick for a sol-gel system, it is not always sufficient for an adhesive. For that purpose, the critical layer thickness is preferably higher, up to about $400 \mu\text{m}$, sometimes even $1000 \mu\text{m}$, as the leads have to be fairly thick for the high currents applied. The shrinkage upon drying and curing of particle filled layers, and the concomitant capillary pressure, is one of the main factors in limiting the layer thickness that can be obtained. The shrinkage can be minimized by removal of liquids before the application as an adhesive. The liquids present may include alcohols, which are either added, or formed in the hydrolysis or alcohol condensation reaction of the sol-gel precursors, water, needed for hydrolysis, and other solvents. An advantageous way of removal of liquids is distillation. After hydrolysis of the sol gel precursor, distillation at a reduced pressure can take place, leaving a concentrated solution in which conductive particles, preferably silver or silver alloy particles can be dispersed. However, the concentrated solution of the sol gel materials in the frequently used alcohol based medium is

often unstable reducing the pot life of the binder. In order to improve the stability of the concentrated solution, it is important to select suitable solvents. It was found that ketones (for example methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone) are especially good solvents for the binder material and can prolong the pot life considerably. Alternative solvents are aromatics such as benzene, toluene, xylenes and others. However, the use of aromatic solvents is not preferred due to their potentially more serious health hazards.

Apart from the benefits in terms of the larger layer thickness that can be obtained by using concentrated binder solution, minimization of evaporation will also reduce the porosity in the layer resulting in stronger bonds.

Using this type of resins that are made of the hybrid sol gel precursors and that are able to soften or melt during curing can make a further improvement. Commercial resins, which have this property, are available and the addition of diphenylsilanediol to the sol-gel formulation also helps in softening or melting during the drying and curing phase. When the sol gel binder melts during the curing process, it aids the evaporation of solvents by increasing their mobility without the formation of voids and it also strongly reduces the build-up of any drying stress. If the coefficient of thermal expansion of the conductive adhesive is matched to that of the substrate, essentially stress-free adhesive deposits can be prepared. The lack of residual stress and match of thermal expansion coefficients then ensures that the adhesive does not crack even in thick layers during temperature cycling. If different substrates are used, the coefficient of thermal expansion of the adhesive can be adjusted in a narrow range by varying the concentration of the conductive metal particles. Obviously, this method has serious limitations, as the electrical conductivity would also be influenced by the variation in the metal particle concentration. An alternative and more general method to adjust the coefficient of thermal expansion is to incorporate a second type of filler that has a much lower coefficient of thermal expansion than that of the conductive particles. Such fillers are ceramic particles such as alumina, silica, boron nitride, silicon carbide and others that have a lower the coefficient of thermal expansion than that of the substrate material. When applying a second type of filler, it is advantageous to limit the particle size of the second filler below 1/10, or more preferably below 1/20, of the particle size of the conductive particles. This size difference then would ensure that the connections between the conductive particles are not blocked by large particles of non-conductive ceramics.

Said formulations are very suitable as adhesives for making the electrical contact of heating elements, especially heating elements made from sol gel materials. By

using a low shrinking sol-gel system in combination with silver particles, a thickness of over 400 µm can be reached, no materials foreign to the sol-gel flat heating systems are introduced, and the silver migration is blocked very effectively by the sol-gel binder. As the materials used in the adhesive and in the conducting layer can be chosen such that they 5 comprise the same particles and sol-gel precursors, no risk of contamination is present, which otherwise could easily change the resistance of the conductive layer. Advantageously, the adhesive can be deposited without pretreatment of the underlying layer. However, pretreatment with for instance an aminosilane or another, preferably silane based, adhesion promoter is optional. The conductive adhesive can be applied before curing said conductive 10 layer, and subsequently be co-cured after care has been taken that most of the solvent has evaporated. The hybrid sol gel precursors used have been shown to effectively reduce the sensitivity to corrosion, thus corrosion at the contact point is not likely to occur. Finally, as the thermal expansion coefficient of the particle filled hybrid sol gel system can be made to closely match that of aluminum, the adhesive is particularly suitable for heating elements 15 made on an aluminum substrate, which is a preferred substrate for heating elements. Although the moisture sensitivity of these materials is low, an additional moisture barrier layer can easily be applied by for instance spray-coating. Especially advantageous compositions comprise sol-gel materials in combination with fluoropolymer particles.

The heat curable adhesive is in particular suitable to be used for making 20 electrical contacts of heating elements for electrical domestic appliance comprises a (steam) iron, ironing device, hair dryers, hair stylers, steamers and steam cleaners, garment cleaners, heated ironing boards, facial steamers, kettles, pressurized boilers for system irons and cleaner, coffee makers, deep fat fryers, rice cookers, sterilizers, hot plates, hot-pots, grills, space heaters, waffle irons, toaster, ovens or water flow heaters.

25 The invention will be further elucidated in the following examples.

Example 1:

49.9 grams of methyltrimethoxysilane, 38.4 grams of methylethylketone, 11.6 grams of water and 0.1 gram of maleic acid were mixed together. The mixture was stirred for 30 2 days, then filtered and placed in a distillation flask. The solvent was partially distilled out at a reduced pressure (700 mbar) and a bath temperature of 80°C. Distillation was continued until the evaporation rate was greatly reduced, such that 37 grams MTMS resin solution was left in the distillation flask out of 100 g present initially.

From this resin solution, a conductive adhesive was prepared using 13.3 grams of the solution, 15.7 grams of methylisobutylketone and 74.2 grams silver flakes followed by the evaporation of another 3.2 g methylethylketone that was part of the MTMS resin solution. Droplets of the adhesive were deposited onto either dried, but not yet cured, or fully cured insulating sol-gel layers on an aluminium substrate. They were found to adhere well after drying at 60-80°C, heating to the curing temperature at a rate less than 10 °C/min (more preferably less than 5 °C/min) and curing for 15 minutes at 415°C. After curing, adhesive droplets with a height of over 1000 µm showed good adhesion and no cracks. The nominal silver content of the cured adhesive was 52 vol%. Its coefficient of thermal expansion, measured parallel to the substrate surface, was approximately 27 ppm/°C, in the range of 125°C to 300°C measured by thermo-mechanical analysis, which is close to that of aluminium.

Example 2:

A commercially available resin, Silres 610 from Wacker was used as a binder. This resin contains methylsiloxane polymers and softens at approximately 80 °C to form a melt. It remains in the liquid form during curing up to about 380 °C, depending on the heating rate. For the adhesive preparation, 7.8 g Silres 610 resin was mixed with 25.4 g methylethylketone (MEK), 7.0 g diisobutylketone and 59.9 g silver flakes. The mixture was milled for over one day using 3 mm glass beads. After the milling, 12.1 g MEK was distilled out to obtain a thixotropic liquid. The liquid adhesive was deposited and cured according to the method described in Example 1. After curing, adhesive droplets with a height of over 1000 µm showed good adhesion and no cracks. The nominal silver content of the cured adhesive was 52 vol%. Its coefficient of thermal expansion, measured parallel to the substrate surface, was approximately 25 ppm/°C in the range of 125°C to 300°C, nearly identical to that of aluminium.

Example 3:

Alumina particles were incorporated into Silres 610 from Wacker. For the adhesive preparation, 6.0 g Silres 610 resin was mixed with 25.2 g methylethylketone (MEK), 6.7 g diisobutylketone, 4.0 g alumina powder and 58.0 g silver flakes. The mixture was milled for over one day using 3 mm glass beads. After the milling, 13.7 g MEK was distilled out to obtain a thixotropic liquid. The liquid adhesive was deposited and cured

according to the method described in Example 1. After curing, adhesive droplets with a height of over 1000 µm showed good adhesion and no cracks. The nominal silver content of the cured adhesive was 52 vol% the remaining 48% binder consisted of 80 vol% sol-gel material and 20 vol% alumina. The coefficient of thermal expansion, measured parallel to the substrate surface, was approximately 23 ppm/°C in the range of 125 to 300°C.

Example 4:

A binder was prepared from TEOS, MTMS and diphenylsilanediol. A mixture of 70.4 g ethanol, 4.8 g water, 0.02 g maleic acid and 2.9 g TEOS was hydrolysed for 10 minutes followed by the addition of 7.7 g MTMS. After a further 10 minutes hydrolysis, 12.1 g diphenylsilanediol was dissolved in the mixture over a period of 15 minutes. As the diphenylsilanediol has a low reactivity under acidic conditions, the catalyst was changed to a base by adding 3.1 g ethanol containing 0.041 g KOH. The mixture was heated to the boiling point and was kept hot for one hour. An oily phase appeared during this period. The mixture was let to cool overnight to form a two phase system of a solid resin and alcohol. The resin was dissolved in toluene and washed with water to remove catalyst residues. After washing, the resin was dried. Experiments indicated that this resin was able to melt during curing similarly to the Silres 610. The solid resin was dissolved in MEK and it was stored as a solution for further use.

For the adhesive preparation, 13.3 g resin solution (containing 55.5% solids) was mixed with 6.1 g diisobutylketone, 21.3 g methylethylketone and 59.3 g silver flakes. The mixture was milled for one day using 3 mm glass beads. After the milling, 26.6 g solvent was distilled out. The liquid adhesive was deposited on glass and cured at 415°C for two hours. After curing, adhesive droplets with a height of over 1000 µm without cracks were formed. The nominal silver content of the cured adhesive was 52 vol%. Its coefficient of thermal expansion, measured parallel to the substrate surface, was approximately 51 ppm/°C in the range 125°C to 300°C.

CLAIMS:

1. An adhesive, suitable for making a electrically conductive connection to a material or system, which is operated at a relatively high temperature, wherein said adhesive is based on a sol-gel precursor.
- 5 2. Adhesive according to claim 1, characterized in that the adhesive is based on a sol gel precursor and metal particles.
3. Adhesive according to claim 1, characterized in that the sol gel precursor comprises hybrid sol gel materials based on methyltri(m)ethoxysilane,
10 phenyltri(m)ethoxysilane, and/or diphenyldi(m)ethoxysilane.
4. Adhesive according to claim 1, characterized in that the conductive particles comprise silver particles or silver alloy particles.
- 15 5. Adhesive according to claim 1 where non-conductive particles with size less than 1/10 of the size of the metal particles are incorporated.
6. Adhesive according to claim 1 where non-conductive particles with size less than 1/20 of the size of the metal particles are incorporated.
- 20 7. Object provided with an adhesive according to claims 1-6, characterized in that the thickness of the adhesive is at least 100 µm.
8. An electrical domestic appliance comprising an adhesive according to claims
25 1-7, characterized in that the electrical domestic appliance comprises a (steam) iron, ironing device, hair dryers, hair stylers, steamers and steam cleaners, garment cleaners, heated ironing boards, facial steamers, kettles, pressurized boilers for system irons and cleaner, coffee makers, deep fat fryers, rice cookers, sterilizers, hot plates, hot-pots, grills, space heaters, waffle irons, toaster, ovens or water flow heaters.

ABSTRACT:

A sol gel material with metal particles, which can be used as a conductive adhesive for systems that have a high operating temperature, is disclosed. The material is especially suitable for appliances equipped with a flat heating element, such as steam irons.